

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
25 March 2004 (25.03.2004)

PCT

(10) International Publication Number  
**WO 2004/024802 A1**

(51) International Patent Classification<sup>7</sup>: C08J 3/205,  
B01J 3/00

(21) International Application Number:  
PCT/GB2003/003964

(22) International Filing Date:  
12 September 2003 (12.09.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
0221150.6 12 September 2002 (12.09.2002) GB

(71) Applicant (*for all designated States except US*):  
SCF PROCESSING LIMITED [IE/IE]; 6 Highfield,  
Drogheda, Co. Louth (IE).

(71) Applicant (*for IS only*): TOLLETT, Ian [GB/GB]; c/o  
Williams Powell, Morley House, 26-30 Holborn Viaduct,  
London EC1A 2BP (GB).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): MATTHEWS,

Siobhan, Olive [IE/IE]; c/o SCF Processing Limited, 6  
Highfield, Drogheda, Co. Louth (IE). MATTHEWS,  
John [IE/IE]; c/o SCF Processing Limited, 6 Highfield,  
Drogheda, Co. Louth (IE).

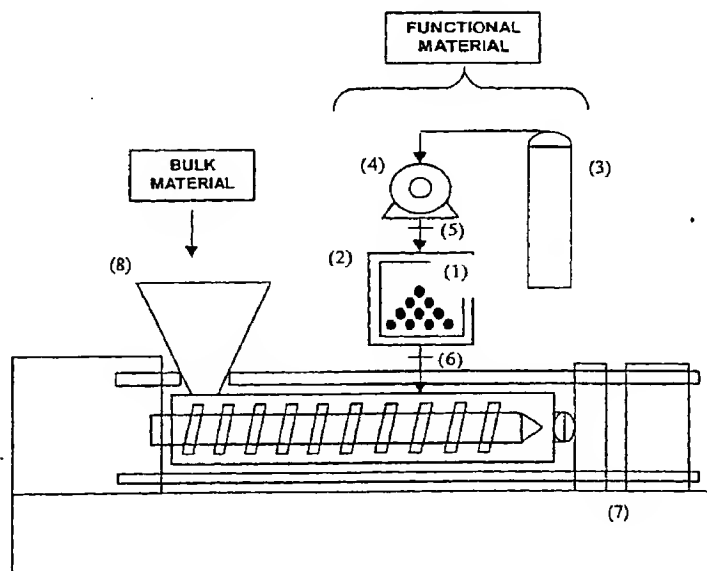
(74) Agents: TOLLETT, Ian et al.; Williams Powell, Morley  
House, 26-30 Holborn Viaduct, London EC1 2BP (GB).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,  
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,  
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,  
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,  
MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC,  
SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA,  
UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),  
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),  
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,  
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,  
SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM,  
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: METHOD OF COMBINING MATERIALS



(57) Abstract: A method for combining materials (such as impregnating materials with functional materials) uses a combination of supercritical fluid technology and polymer melt processing technology. The functional material is soluble in a near supercritical or supercritical fluid, which dissolves in the matrix/bulk material during melt processing. Controlling the processing conditions facilitates a change of state for the fluid, which results in the precipitation of the functional material in the bulk material. The impregnated bulk material may be shaped using conventional polymer based processing techniques such as extrusion and injection moulding.

**Published:**

— with international search report

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

### Method of Combining Materials

The present invention relates in general to a method for combining a first material and a second material and in particular to a method for incorporating functional materials into bulk material systems.

- 5 A functional material is a material that has the ability to perform a specific function or a number of functions. By incorporating a functional material into a bulk material the resultant material system can have the ability to undertake the specific function or functions without adversely affecting the original properties of the bulk material. Therefore, bulk materials, both inorganic and organic such as polymers, ceramics, metals  
10 and wood, can be processed in such a way that functional materials can be incorporated into the matrix.

Functional materials could for example impart useful properties to the bulk material such as the ability to transmit and/or receive electrical, microwave and radio wave signals. Other functions which could be imparted include the ability to absorb and/or transmit  
15 energy from the electromagnetic spectrum, sound energy, an electrical charge or heat. In addition, mechanical properties such as impact resistance and burst strength could be enhanced. After mixing and shaping the bulk material could act as a chemical or biological sensor.

Conventional polymer based melt processing facilitates the incorporation of materials such  
20 as fillers into a matrix material at a macroscopic level.

Methods employed include

- (i) dry mixing of the filler and the matrix material prior to melt processing

Step 1: weigh materials

Step 2: place weighed materials in blender (eg V-blender) for dry mixing

- 25 Step 3: place dry blend in polymer melt processing equipment for melt mixing, shaping in die or mould section and then solidification.

A schematic of type (i) conventional processing is provided in Figure 1:

- (ii) adding the filler to the polymer melt (matrix) during compounding (form of extrusion)

Step 1: weigh materials

Step 2: place weighed matrix/bulk materials in polymer melt processing equipment

Step 3: add filler/functional material downstream via feed port in barrel of extruder or injection moulder for melt mixing, shaping in die or mould section and then solidification.

- 10 A schematic of type (ii) conventional processing is provided in Figure 2.

Conventional techniques include melt, mix, blend and shaping, extrusion, injection moulding, blow moulding, vacuum forming or thermoforming, multi layer extrusion, multi shot injection moulding, rotational moulding and blown film extrusion.

15

In conventional polymer-based melt processing, fillers might be chosen to enhance the mechanical properties of the matrix material, to reduce material cost or to provide aesthetic qualities. However, these fillers might affect the aesthetic properties or the anisotropy of the matrix material or the material system. Also if the distribution is not efficient the function of the filler might not be effective!

20

To date the incorporation of functional materials into bulk systems using conventional polymer melt processing techniques other than for mechanical enhancement, to reduce material cost or to provide aesthetic qualities is rare.

25

It is well known that supercritical fluids such as supercritical carbon dioxide can behave as tuneable solvents and provide a clean and efficient method for the extraction of components from bulk materials such as soil remediation and the decaffeination of coffee (as disclosed in US 3,806,619).

- 30 Supercritical fluids can also be used in the processing of materials as disclosed in WO 02/47893 (Brunel University). This method employs a supercritical or near-supercritical

fluid for the processing of polymer formulations without induced foaming, resulting in the benefits of reduced melt viscosity and/or lower melt temperatures.

A number of techniques have been developed whereby a supercritical fluid is employed to swell a polymer matrix and to impregnate the matrix with a specific material. Supercritical  
5 fluids have been used for example to dye batch materials in their solid state. When the conditions are altered so that the fluid becomes gaseous it leaves the solid polymer leaving the dye within the swelled polymer cavity. A good review of such methods can be found in Kazarian "Polymer Processing with Supercritical Fluids" *Polymer Science, Ser. C, Vol. 42, No. 1, 2000, pp. 78-101*. Another review is given by Cooper in "Polymer synthesis and  
10 processing using supercritical carbon dioxide" *J. Mater. Chem., 2000, 10, 207-234*.

US 5,508,060 (Minnesota Mining and Manufacturing Company) describes a method for impregnating various polymer substrates with an impregnation additive by simultaneously contacting the polymer substrate with a supercritical fluid, an impregnation additive (which is substantially insoluble in the supercritical fluid) and a carrier liquid.

15 US 6,051,174 (Massachusetts Institute of Technology) discloses the use of a supercritical fluid as a blowing agent in polymer melt processing to form microcellular foamed components. During processing the blowing agent dissolves into the bulk material to form a single phase. However, no functional materials are introduced into the polymer.

No bulk polymer-based material processing technique (for example extrusion or injection  
20 moulding) enabling the addition of materials at a nanoscale or near nanoscale level has been reported.

The present invention seeks to provide an improved method and system for incorporating functional materials into bulk materials. It uses conventional polymer processing techniques allied with unique and novel processing to allow products with functional  
25 applications having complex geometries and no size restrictions to be manufactured on a commercial scale. The invention provides a clean, efficient and environmentally friendly method for the incorporation of functional materials.

According to a first aspect of the present invention, there is provided a method for

combining a first material and a second material, comprising the steps of providing a fluid which is near or in the supercritical fluid state, forming a single phase solution from the first material, the second material and said fluid, and removing said fluid from said solution in order to leave the combined first and second materials.

5

The first material may be at least partially dissolved in said fluid before the second material or *vice versa*. Alternatively, the first material may be dissolved in said fluid and then the resulting solution dissolved in the second material, if the second material is in a molten or semi-solid state. It will be appreciated that it is not always clear on a molecular level which component is dissolving in which; the important thing however is that a single phase solution of the three components is formed.

10

The first material is preferably a functional material, that is a material which alters the function of the second material. Examples of functional materials include minerals, vitamins, fullerenes, metals, non-metals, herbs, naturally occurring materials, caffeine, organic materials, plastics materials, monomers, oligomers, polymers, or any combination thereof.

15

Functional materials can be used for micro-devices, data storage, light emitting diodes, photovoltaic cells, fuel cells, batteries and tissue engineering applications. It is possible to enhance the electrical, optical, magnetic, mechanical, energy transfer and chemical sensory properties of bulk materials using this new technology. The teachings herein enable conventional processing equipment to shape complex functional parts and improve on the present small batch scale production limitations.

20

Particularly preferred uses of the present invention include:

25

1. The incorporation of food additives such as vitamins and minerals into foodstuffs.
2. The incorporation of herbs, minerals and vitamins into personal hygiene products such as cosmetics, shampoos, conditioners, creams and lotions.
3. The incorporation of a conductive material into the body of a mobile telephone to form an antenna.

4. The incorporation of a radio-frequency transmitter into a helmet for tracking military personnel.
5. Forming an LCD display in a helmet visor.
6. Toughening structures such as glass, concrete and ceramics by incorporating strengthening materials such as buckminsterfullerene.
7. Incorporating dyes and/or fluorescent materials in buildings, aircraft, automobiles, protective clothing, footwear, and protective headwear such as crash helmets, that allow visual warning if an impact has exceeded a predetermined limit and therefore the structural integrity of the component has been compromised.
8. Incorporating functional materials such as nanoclays in petroleum containers to restrict or retard the leakage of vapours from the containers.
9. Toughening protective clothing such as stab proof vests and bullet proof vests by incorporating energy absorbing materials and strengthening materials such as nanoclays and other nanomaterials.
10. Incorporating materials such as lead that block the transmission of energy, such as sound, electrical and thermal energy from buildings, structures and clothing.
11. Incorporating conductive materials such as copper in flexible materials to reduce the size and improve the design of solar panels.
12. Incorporating silicon materials in polymer materials so that flexible silicon chips can be manufactured.
13. Improving bone graft growth by incorporating growth active materials such as phosphorous throughout the temporary bone scaffold.
14. Improving the extraction efficiency of polymer based binder formulations and allowing the formation of open porous structures on-demand from metal and ceramic shaped components (green state) by incorporating surfactants in the formulation during shaping prior to debinding by supercritical fluid extraction and sintering.

15. Improving the flame retardant properties of polymers and textiles by incorporating flame retardant materials such as magnesium hydroxide throughout the body of the component.

According to a further aspect of the present invention, there is provided a method of  
5 incorporating into a bulk material a functional material, including the steps of dissolving at least one functional material, in part or in full, in a fluid, which fluid is near or in the supercritical fluid state, and adding the solution of functional material into a bulk material provided in a semi-solid or molten state.

This can be achieved by a variety of methods. The supercritical fluid or near supercritical  
10 fluid acts as a solvent and may include the use of entrainers, co-solvents, ligands, and other binding agents such as enzymes and receptors. This method may also include the step of maintaining the system above a predetermined temperature or pressure and the use of more than one supercritical fluid.

The usual definition that is given of a supercritical fluid is a substance where the  
15 conditions are such that the temperature and pressure of the substance are both above the critical values. The liquid phase and the gaseous phase are in equilibrium and the transition between them is continuous. However, as is pointed out in the Cooper article referred to above, this definition gives no information about the density of the substance. Cooper therefore quotes a more accurate definition by Darr and Poliakoff, in which a  
20 supercritical fluid is described as

“any substance, the temperature and pressure of which are higher than their critical values, and which has a density close to or higher than its critical density”.

As is explained by Cooper, many applications of supercritical fluids (SCFs), particularly carbon dioxide, require conditions of temperature and pressure such that the density  
25 exceeds the critical density, so that the SCF may have properties intermediate between a liquid and a gas. To quote from Cooper:

“When a liquid is heated above its critical temperature at pressures in excess of the critical pressure the transition from liquid to supercritical fluid is continuous ...



unlike the discontinuous transition from liquid to gas when a substance boils at pressures below  $P_c$ . Hence, under the appropriate conditions (i.e., slightly below the critical temperature and pressure), liquid  $\text{CO}_2$  may be considered as a “near-critical” fluid. This means that, while being a liquid, the substance may exhibit some SCF-like properties such as reduced viscosity and density. As a consequence, near-critical liquid  $\text{CO}_2$  displays a limited degree of compressibility and its solvent properties may be fine-tuned with pressure, albeit to a much lesser extent than in the supercritical state. A practical advantage of working with liquid  $\text{CO}_2$  is that relatively high solvent densities can be achieved at moderate pressures: for example, the density of liquid  $\text{CO}_2$  at  $20^\circ\text{C}$  is greater than  $0.84\text{ g cm}^{-3}$  at pressures above 75 bar. For certain processes that operate near the critical temperature for  $\text{CO}_2$  ( $31.1^\circ\text{C}$ ) one may be able to choose between working with  $\text{CO}_2$  in the liquid state or under supercritical conditions. In such cases the best choice will be determined by the specific process requirements.”

Thus the present invention encompasses the use of fluids in the near-supercritical state as well as in the supercritical state.

In practice, those skilled in the art will be able to judge when the fluid is in the appropriate state by the conventional viewing of the cloud point. This technique utilises a pressure vessel with viewing windows in which a fluid can be subjected to temperature and pressure variation to induce the supercritical or near-supercritical state. Prior to achieving the supercritical fluid state when the transition between liquid and gas becomes continuous the contents of the vessel are viewed as cloudy.

A list of SCFs which are suitable for use in the present invention is provided in Table 1 below, which is taken from the Cooper reference. In the Table,  $T_c$  = critical temperature,  $P_c$  = critical pressure and  $\rho_c$  = critical density (the density at the critical temperature and pressure).

Table 1

|    | <u>Substance</u>              | <u>T<sub>c</sub>/°C</u> | <u>P<sub>c</sub>/bar</u> | <u>ρ<sub>c</sub>/g cm<sup>-3</sup></u> |
|----|-------------------------------|-------------------------|--------------------------|--|
| 5  | CH <sub>4</sub>               | -82.5                   | 46.4                     | 0.16                                   |
|    | C <sub>2</sub> H <sub>4</sub> | 10.0                    | 51.2                     | 0.22                                   |
|    | C <sub>2</sub> F <sub>6</sub> | 19.9                    | 30.6                     | 0.62                                   |
|    | CHF <sub>3</sub>              | 26.2                    | 48.5                     | 0.62                                   |
|    | CClF <sub>3</sub>             | 28.9                    | 38.6                     | 0.58                                   |
| 10 | CO <sub>2</sub>               | 31.1                    | 73.8                     | 0.47                                   |
|    | C <sub>2</sub> H <sub>6</sub> | 32.4                    | 48.8                     | 0.20                                   |
|    | SF <sub>6</sub>               | 45.6                    | 37.2                     | 0.73                                   |
|    | Propylene                     | 91.9                    | 46.1                     | 0.24                                   |
|    | Propane                       | 97.2                    | 42.5                     | 0.22                                   |
| 15 | NH <sub>3</sub>               | 132.5                   | 112.8                    | 0.24                                   |
|    | Pentane                       | 187.1                   | 33.7                     | 0.23                                   |
|    | <sup>i</sup> PrOH             | 235.4                   | 47.6                     | 0.27                                   |
|    | MeOH                          | 240.6                   | 79.9                     | 0.27                                   |
|    | EtOH                          | 243.5                   | 63.8                     | 0.28                                   |
| 20 | <sup>i</sup> BuOH             | 275.1                   | 43.0                     | 0.27                                   |
|    | Benzene                       | 289.0                   | 48.9                     | 0.30                                   |
|    | Pyridine                      | 347.1                   | 56.3                     | 0.31                                   |
|    | H <sub>2</sub> O              | 374.2                   | 220.5                    | 0.32                                   |

- 25 As Kazarian points out, the definition of a supercritical state only applies to a pure substance, as do the figures in Table 1 above. If for example a co-solvent is added to a fluid then this can reduce the pressure at which the fluid becomes supercritical. Any suitable co-solvents may be employed, and these include (but are not limited to) methanol, ethanol, propanol, propylene carbonate, butyl alcohol, propylene carbonate, toluene, pentane, acetylacetone, octane, acetone or any combination thereof. The proportion of co-solvent to said fluid may be as low as 1:100 and is preferably about 1:20, although if necessary the proportion can rise to 1:1.

The preferred embodiment adds sufficient fluid in the near or supercritical state to allow the dissolution of the functional material in the fluid. The preferred embodiment includes means to control the amount of functional fluid/solution that is incorporated into the bulk molten or semi-solid material.

Thus, in the preferred embodiment, functional materials can be dissolved into supercritical

and near supercritical fluids and the "mixture" then formed is then incorporated into the bulk material during processing. A typical process would involve a polymer melt processing technique such as injection moulding or extrusion, blow moulding, vacuum forming or thermoforming, multi layer extrusion, multi shot injection moulding, rotational moulding, blown film extrusion where the bulk material is melt mixed and then shaped before solidification. Examples of supercritical fluid assisted processing, without the impregnation of functional materials, are described in WO 02/47893, the contents of which are incorporated herein by reference. During processing the functional material solution dissolves into the bulk material. Altering the solution conditions such as temperature and pressure facilitates precipitation of the functional material from the solution.

In a preferred embodiment the supercritical fluid is injected into a first vessel to contact the functional material and form a functional fluid. The functional fluid is then injected into polymer melt processing equipment where it is combined with the bulk material to form a single phase solution. This could be done manually, but for product consistency it is preferably to control each operation accurately and be co-ordinated or synchronised with the polymer melt process.

Accordingly, gravimetric or volumetric hopper feeders may be used to control the delivery of the bulk material to the processing machine. These feeders are linked to the process control unit of processing machine and therefore can precisely feed the bulk material.

Electronic actuators that are linked to the processing machine, the syringe pumps, pressure transducers and temperature probes in the pressure vessels control the opening and closing of the valves which ultimately feed the functional solution into the processing machine. This allows the precise quantity of functional solution to be injected into the polymer processing equipment.

A specially designed one-way valve allows the injection of the functional solution into the polymer processing machine and avoids blockages occurring at the injection point. An electronic actuator operates this valve.

During an injection moulding type process the injection of the functional solution is synchronised with the plasticizing step

These are indications of how to achieve precise control and metering of the functional solution. A person skilled in the art could provide improvements to this process. For example as with all polymer processing operations/techniques each process should be optimised and is subject to a variety of variables such as the material(s) to be processed  
5 and the processing conditions. In the case of extrusion based techniques material feed rate, barrel temperature, screw profile(s), screw lengths, shear rate, die design, die temperature and die pressure. The variables for injection moulding based techniques include barrel temperature, screw profile(s), plasticizing duration, changeover point from dosing to injection, injection pressure, injection speed, shot size, cushion size, holding pressure,  
10 holding time, back pressure, moulding design, mould clamping force, mould clamping time and pressure levels in the mould.

Variables that are specific to supercritical fluid-assisted polymer processing include but are not limited to the bulk/matrix material, the functional material and its solubility in the supercritical fluid(s), the formation of a single phase solution, the dose rate of the bulk and  
15 functional materials, the injection point of the functional solution, the processing temperatures, processing pressures such as in the barrel, mould and die, the shear rate and the shear stress developed during the manufacturing process.

The supercritical or near supercritical fluid can be recycled and used again or can be vented to atmosphere.

20 In a particularly preferred embodiment the second material is not swollen by the supercritical fluid, and is preferably not swollen at all during the method.

One suitable fluid is carbon dioxide but the invention is not limited to this fluid. Other fluids such as water and nitrogen could be used or any of the fluids listed in Table 1 above, either alone or in combination.

25 According to another aspect of the present invention, there is provided apparatus for incorporating into a bulk material a functional material, including means for providing at least one functional material, means operable to provide a fluid at a supercritical or near supercritical state, means for dissolving, in part or in full, said at least one functional material in said fluid, and means operable to add the solution of functional material into a

bulk material provided in a semi-solid or molten state.

The preferred embodiment uses provides a processing technique which can be incorporated into conventional processes, for example polymer-based processing such as extrusion and injection moulding, to manufacture products with functional applications. The preferred  
5   embodiments can provide a clean, efficient and environmentally friendly method for the incorporation of functional materials of the types outlined above and other functional materials which can impart useful properties to the matrix material, such as to transmit and/or receive electrical, microwave and radio wave signals. The absorption and/or the transmission of energy from the electromagnetic spectrum, sound energy, an electrical  
10   charge and heat or the bulk material to act as a chemical or biological sensor can also be accomplished using the techniques disclosed herein, as they can provide a new method for the incorporation of functional materials into the bulk material system.

A number of preferred embodiments of the present invention are described below, by way of example only, with reference to the accompanying drawings, in which:

15       Figure 1 is a flow diagram of a prior art process for incorporating a filler into a bulk material;

Figure 2 is a flow diagram of an alternative prior art process for incorporating a filler into a bulk material;

Figure 3 shows one embodiment of system in accordance with the invention for  
20   incorporating into a bulk material one or more functional materials; and

Figure 4 shows another embodiment of system in accordance with the invention for incorporating into a bulk material one or more functional materials.

Figure 3 outlines one possible embodiment of the invention. The functional material (1) is placed in a vessel containing sight glasses where the pressure and temperature can be  
25   controlled (2). The fluid (3) is fed to a pump capable of achieving high pressures (4). In this embodiment, the pump used is an ISCO 260D syringe pump (obtainable from ISCO Inc., Nebraska, USA). Under the correct operating conditions of pressure and temperature the fluid reaches its supercritical or near supercritical state. This fluid is injected into the

pressure vessel (2) using an electronically actuated valve (5).

Using carbon dioxide as an example under the correct operating conditions of pressure and temperature the fluid reaches its supercritical or near supercritical state dissolving the functional material (850 to 5000 psi and from 30 °C). Some functional materials might require the addition of entrainers, co-solvents, ligands, and other binding agents such as enzymes and receptors depending on the solubility of the functional material in the supercritical fluid.

10 This functional solution is then injected into polymer melt processing equipment using an electronically controlled specially designed one-way valve (6). Injection can be assisted using a second pump. Whilst the functional solution is being injected into the polymer melt processing equipment (7), the bulk material is fed via the hopper (8).

15 As the bulk material is fed downstream the material is heated and sheared so that when the functional solution is fed into the machine the majority of the bulk material is in its melt state. When the functional material is injected into the bulk material a single-phase solution is formed. The formation of this solution could be aided by mixing sections in the machine. The functional fluid can be injected in any position in the machine for example, via a hopper (using a pressurised and sealed hopper), in the heated barrel which contains the rotating screw(s), in the die section in the case of extrusion based equipment, in the nozzle section that feeds the mould in the case of injection moulding based equipment and in the runner sections in the mould.

25 In all cases the majority of the bulk material has to be in its melt state and mechanical mixing or sufficient turbulence is introduced to allow the formation of a single-phase functional solution.

Another possible embodiment of this invention is outlined in Figure 4. The functional material (1) is placed in a vessel containing sight glasses where the pressure and temperature can be controlled (2). The fluid (3) is fed to a pump capable of achieving high pressures (4). The pump used in this embodiment is an ISCO 260D syringe pump (ISCO

Inc., Nebraska, USA). Under the correct operating conditions of pressure and temperature the fluid reaches its supercritical or near supercritical state, this fluid is injected into the pressure vessel (2) using an electronically actuated valve (5). Using carbon dioxide as an example under the correct operating conditions of pressure and temperature the fluid reaches its supercritical or near supercritical state dissolving the functional material (850 to 5000 psi and from 30 °C). Some functional materials might require the addition of entrainers, co-solvents, ligands, and other binding agents such as enzymes and receptors depending on the solubility of the functional material in the supercritical fluid. This functional solution is then injected into a pressure chamber (9) for semi-solid impregnation.

The functional material is soluble in a near supercritical or supercritical fluid, which dissolves in the matrix material. Alternation of the processing conditions facilitates a change of state for the fluid, which results in the precipitation of the functional material in the bulk material. This method allows the shaping of the impregnated bulk material using conventional polymer based processing techniques such as extrusion and injection moulding.

In some embodiments the functional material could aid the removal of certain unwanted materials after bulk processing. For example a material formulation might be used to facilitate shaping of components but is not required after shaping or it could be detrimental to the success of additional processing steps that are required. In another example the removal of a material after processing would enhance the formation of an open porous or interconnected network. The functional material could also aid the removal of unwanted materials that are used to enhance processing or are present as a result of processing (processing by-products), without such removal overall properties of the finished product could be affected. In all cases this type of functional material will increase the efficiency of extraction.

A number of Examples will now be described.

#### **EXAMPLE 1: The incorporation/impregnation of vitamins into bulk materials**

Liposoluble vitamins such as vitamin A, D and E can be impregnated into bulk materials

such as food, body lotions, creams and cosmetics. In this example vitamin E ( $\alpha$ -Tocopherol acetate, Sigma-Aldrich, Dorset, UK), i.e. the functional material was placed in a SS316 vessel capable of withstanding high pressures (300B vessel, SCF Processing Ltd, Ireland) and methanol (99% purity, BDH, Poole, England) was added before the vessel  
5 was sealed. Liquid CO<sub>2</sub> (BOC, Dublin, Ireland) was injected into the vessel and the vessel was pressurised to 5,000psi 80°C using an Isco 260D syringe pump. When the vitamin E dissolved in the CO<sub>2</sub>/methanol, 2wt% of this functional solution was injected into a twin-screw at 80°C and 2,000psi extruder containing water, stearic acid, cetyl alcohol, potassium chloride and extruded at 90°C. The pressure was reduced to atmospheric  
10 pressure on exiting the die, the methanol and CO<sub>2</sub> were vented.

#### Modification: A

The vitamin E and methanol were placed in a container overnight prior to pressurisation.

#### Modification: B

The functional solution was prepared as outlined in Example 1 and then injected into a  
15 second vessel containing water, stearic acid, cetyl alcohol and potassium chloride. This vessel was pressurised and heated to 80°C and the contents of the vessel were mixed using a high-pressure mechanical mixing attachment. A single-phase solution was formed and mixing continued for 20 mins. The pressure was reduced gradually to atmospheric pressure, the methanol and CO<sub>2</sub> were vented and the contents of the vessel were removed.

#### 20 Modification: C

14ml of Methanol was placed in the syringe pump & the 266ml capacity pump was filled with liquid CO<sub>2</sub>. The pump was pressurised to 5,000psi at 80°C and this solution was then injected into the vessel containing the vitamin E. The vessel was pressurised to 5,000psi at 80°C and the solution was mixed. The solution was then transferred to a second vessel  
25 containing the water, stearic acid, cetyl alcohol, potassium chloride, as outlined in example 1 Modification B.



**EXAMPLE 2: Fullerenes impregnated into polystyrene.**

Buckminsterfullerene powder ( $C_{60}$ ) (BDH, Poole, England), i.e. the functional material was placed into a pressure vessel (300B vessel, SCF Processing Ltd, Ireland). Toluene (>99% purity, Romil Ltd. Cambridge, England) was also placed in the vessel. Liquid  $CO_2$  was injected into the vessel and the vessel was pressurised to 3,000psi at 50°C using an Isco 260D syringe pump. When the fullerene powder dissolved in the  $CO_2$ /toluene, 2 wt% of the functional solution was injected at 2,500psi and 150°C into a twin screw extruder that was melt processing polystyrene. The fullerene/toluene/ $CO_2$  solution dissolved into the molten polymer and a single-phase solution was formed. By altering the pressure in the extruder and/or by exiting the die the  $CO_2$ /toluene was vented off leaving the fullerene, the functional material impregnated in the polystyrene.

**Modification: A**

As Example 2 but the fullerene and toluene were placed in a container overnight prior to pressurisation and treatment.

**15 Modification: B**

The functional solution was pumped into a second pressure vessel that contained polystyrene powder (Ashland, Alfreton, England) and mixed at 150°C at 2,500psi using a high-pressure mechanical mixing attachment. Mixing continued for 20 mins once a single-phase solution was formed. The pressure was reduced gradually to atmospheric pressure by venting. When the vessel cooled sufficiently the polystyrene impregnated with fullerene was removed.

**EXAMPLE 3: Impregnating copper into polymers**

Copper powder (Lab Pak Ltd, Fillongley, UK), i.e. the functional material was placed in a vessel capable of withstanding high pressures (300B vessel, SCF Processing Ltd, Ireland) and acetylacetone (chelating agent) was added before the vessel was sealed. Liquid  $CO_2$  was injected into the vessel and the vessel was pressurised to 2500 psi at 150°C using an Isco 260D syringe pump. When the powder dissolved in the  $CO_2$ /acetylacetone, 2wt% of the functional solution was injected at 150°C and 2500 psi into an injection moulding

machine that was melt processing polystyrene. The functional solution dissolved in the polymer melt and after sufficient mixing a single phase solution was formed. A standard injection moulding operation was performed after this.

**EXAMPLE 4: Drying of wood fibres prior to melt processing of polymer/wood  
5 composites**

If moisture is present in wood fibres/flour problems are encountered during melt processing (eg extrusion, injection moulding) of wood/polymer composites.

Wood fibres were placed in the 300B vessel and the vessel was sealed. Methanol was injected into the vessel at room temperature and 300psi using an Isco 260 D syringe pump.

10 The vessel remained pressurised for 60mins prior to venting. This technique was repeated four more times. When the vessel was vented for the fourth time methanol at room temperature was injected until the methanol covered the wood fibres and this was left overnight. The wood fibres were then removed and the excess methanol was dried off with a tissue. The fibres were then returned to the pressure vessel, CO<sub>2</sub> at 35°C and 2,000psi  
15 was injected into the vessel. After 60mins of treatment the CO<sub>2</sub> was vented off and the CO<sub>2</sub> treatment was repeated. The dried wood fibres were removed from the vessel. At this stage in the process the wood moisture free wood fibres could be sealed in a bag and stored prior to use. Alternatively the fibres can be directly fed into a twin screw extruder and compounded with a polymer melt such as polypropylene or polystyrene.

20 In this example methanol the functional material replaces moisture in the wood fibres and the CO<sub>2</sub> dissolves the methanol.

CLAIMS

1. A method for combining a first material and a second material, comprising the steps of  
providing a fluid which is near or in the supercritical fluid state,  
5 forming a single phase solution from the first material, the second material and said fluid, and  
removing said fluid from said solution in order to leave the combined first and second materials.
- 10 2. A method as claimed in claim 1, wherein the first material is at least partially dissolved in said fluid and then the second material is dissolved in said fluid.
3. A method as claimed in claim 1, wherein the second material is at least partially dissolved in said fluid and then the first material is dissolved in said fluid.
- 15 4. A method as claimed in any preceding claim, wherein the second material is provided in a semi-solid or molten state.
5. A method as claimed in any preceding claim, wherein the fluid is removed from  
20 said solution by reducing the pressure in order to vent the fluid to atmosphere as a gas.
6. A method as claimed in any preceding claim, wherein the fluid is removed from said solution by suction.
- 25 7. A method as claimed in any preceding claim, wherein the fluid is carbon dioxide, water, nitrogen or any combination thereof.
8. A method as claimed in any preceding claim, wherein said solution is processed in order to produce a final product.
- 30 9. A method as claimed in claim 8, wherein the processing is extrusion or injection

moulding.

10. A method as claimed in any preceding claim, wherein the first material is a material which alters the function of the second material.

5

11. A method as claimed in any preceding claim, wherein the first material comprises a mineral, a vitamin, a fullerene, a metal, a non-metal, a herb, a naturally occurring material, caffeine, an organic material, a plastics material, a monomer, an oligomer, a polymer, or any combination thereof.

10

12. A method as claimed in any preceding claim, wherein a co-solvent is added to said fluid either before, after or during the formation of said single phase solution.

13. A method as claimed in claim 12, wherein the proportion of co-solvent to said fluid is about 1:20.

15

14. A method as claimed in claim 12 or 13, wherein the co-solvent comprises methanol, ethanol, propanol, butyl alcohol, propylene carbonate, toluene, pentane, acetylacetone, octane, acetone or any combination thereof.

20

15. A method as claimed in any preceding claim, wherein the second material comprises a polymer, a ceramic, a metal or wood.

16. Apparatus for combining a first material and a second material, including means operable to provide a fluid at a supercritical or near supercritical state, means for forming a single phase solution from a first material, a second material and said fluid, and means for removing said fluid from said solution in order to leave the combined first and second materials.

25

1/4

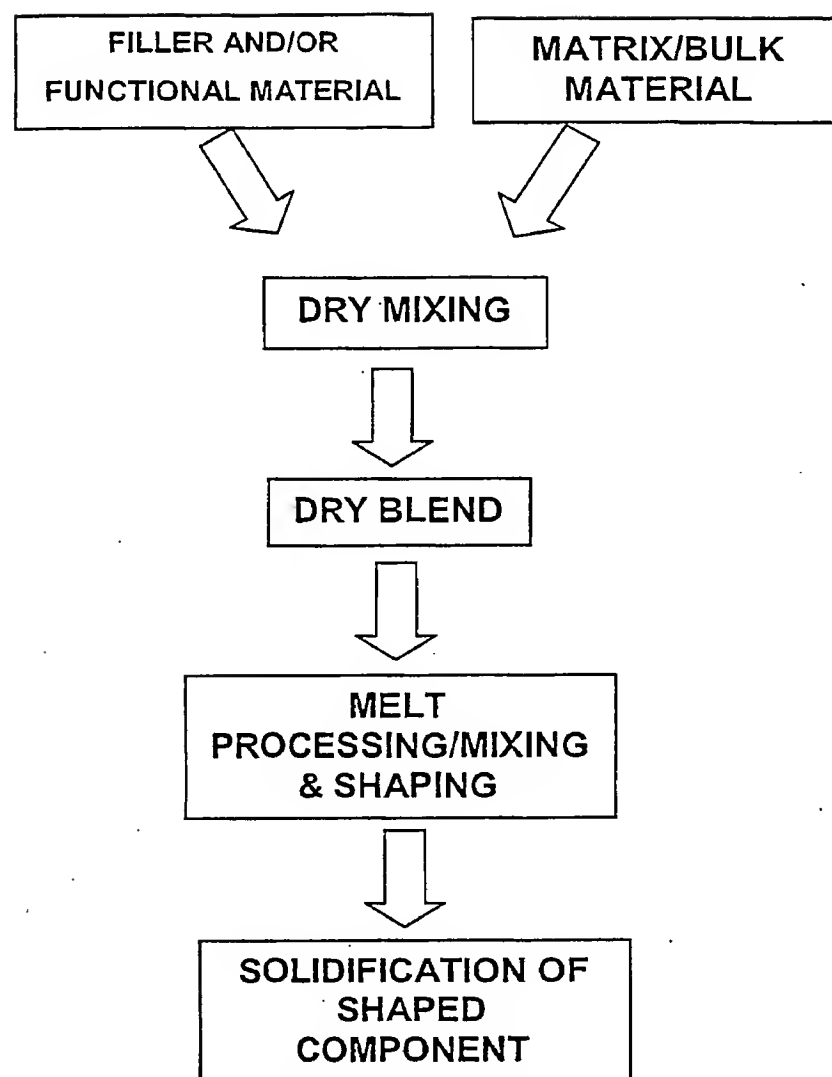


Figure 1

2/4

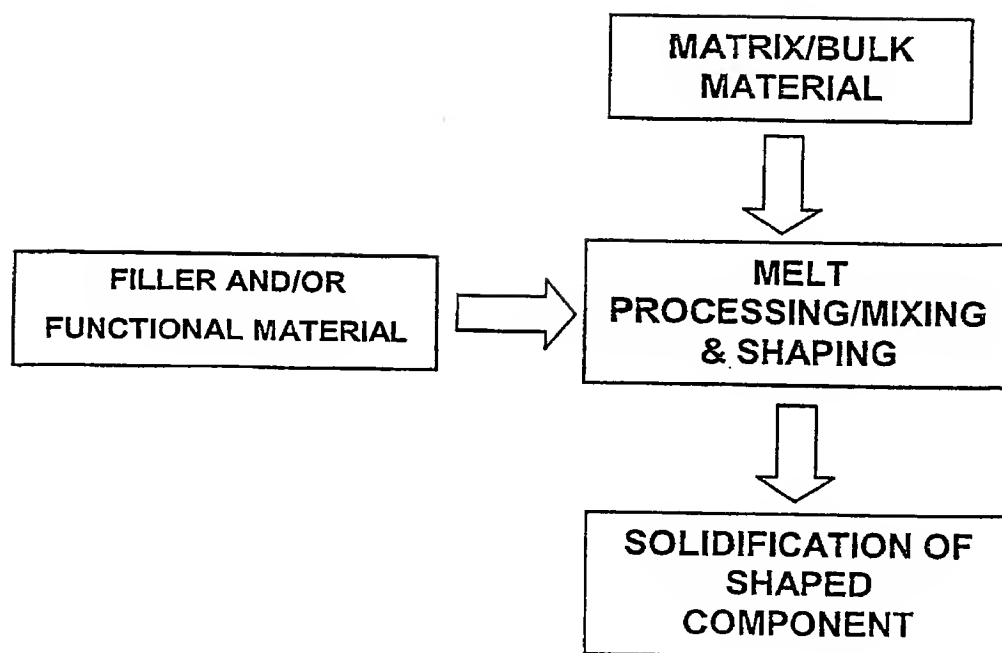


Figure 2

3/4

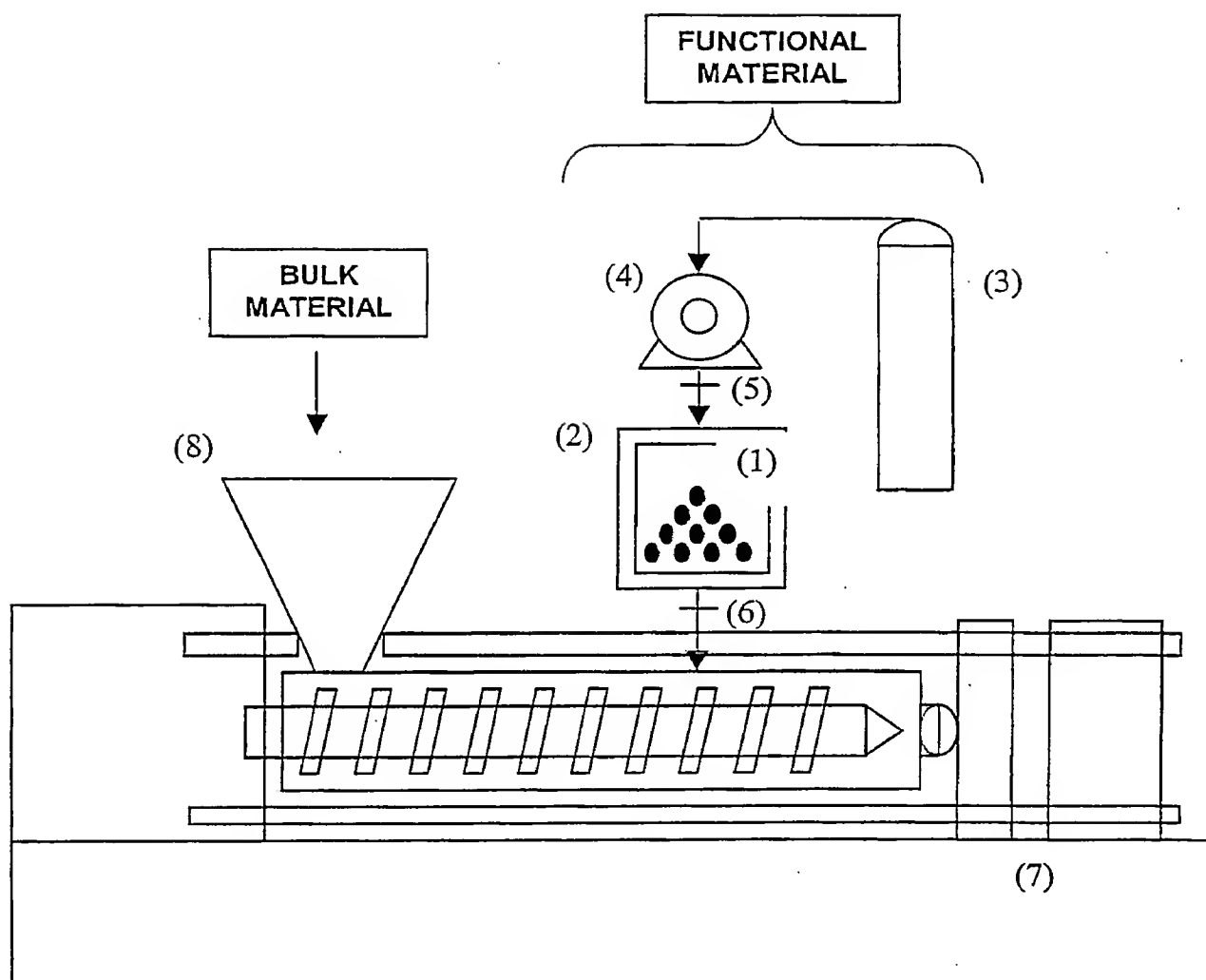
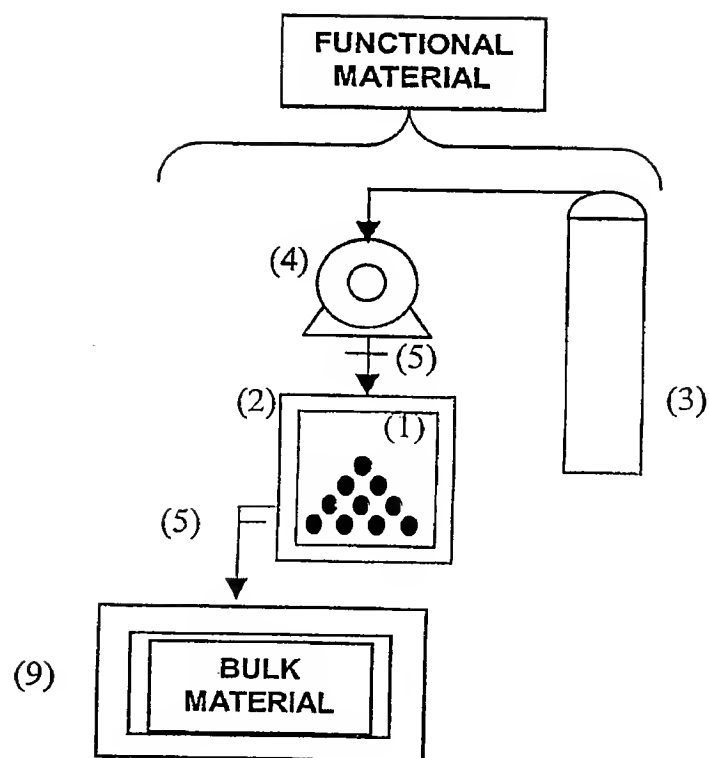


Figure 3

Figure 4





## INTERNATIONAL SEARCH REPORT

Internal Application No

PCT/GB 03/03964

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C08J3/205 B01J3/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08J B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No. |
|------------|---|-----------------------|
| X          | US 5 866 053 A (PARK CHUL B ET AL)<br>2 February 1999 (1999-02-02)<br>column 3, line 17 -column 11, line 35;<br>claim 8; figures  | 1-11, 15,<br>16       |
| X          | WO 96 00610 A (HANNA MAZEN ; UNIV BRADFORD<br>(GB); YORK PETER (GB))<br>11 January 1996 (1996-01-11)<br>page 6, line 19 -page 7, line 18<br>page 10, line 30-35<br>page 12, line 6 -page 13, line 10<br>page 15, line 5-17<br>page 19, line 6-23<br>page 20, line 9 -page 21, line 2<br>page 24, line 11 -page 29, line 23;<br>figures<br>page 43, line 23-27; claims; examples | 1-7,<br>10-16         |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*&\* document member of the same patent family

Date of the actual completion of the international search

5 December 2003

Date of mailing of the international search report

19/12/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5618 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Otegui Rebollo, J

## INTERNATIONAL SEARCH REPORT

Internat. Application No

PCT/GB 03/03964

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No.  |
|------------|--|------------------------|
| X          | WO 01 97584 A (DU PONT)<br>20 December 2001 (2001-12-20)<br>page 2, line 2 -page 4, line 22<br>page 5, line 13-28; claims; figures;<br>example   | 1-11, 15,<br>16        |
| X          | WO 94 09913 A (FERRO CORP)<br>11 May 1994 (1994-05-11)<br>page 3, line 14 -page 4, line 27<br>page 5, line 12 -page 16, line 11; claims  | 1-8, 10,<br>11, 15, 16 |
| X          | US 2002/090458 A1 (MCCULLOUGH KENNETH JOHN<br>ET AL) 11 July 2002 (2002-07-11)<br>paragraph '0002!<br>paragraph '0011! - paragraph '0020!;<br>claims   | 1-8,<br>10-16          |
| X          | EP 0 370 268 A (UNION CARBIDE CHEM<br>PLASTIC) 30 May 1990 (1990-05-30)<br>page 5, line 33 -page 12, line 35; claims;<br>figures; examples   | 1-5, 7, 8,<br>10-16    |
| X          | EP 0 590 647 A (UNION CARBIDE CHEM<br>PLASTIC) 6 April 1994 (1994-04-06)<br>page 3, line 16 -page 7, line 56; claims;<br>figures; examples 3, 12, 13   | 1-16                   |
| X          | WO 93 06731 A (CORNELL RES FOUNDATION INC)<br>15 April 1993 (1993-04-15)<br>page 2, line 11 -page 12, line 20; claims;<br>figure; example  | 1-16                   |
| X          | US 5 417 992 A (MULVANEY STEVEN ET AL)<br>23 May 1995 (1995-05-23)<br>column 3, line 18 -column 6, line 57<br>column 8, line 1-28; claims; figures   | 1-11, 15,<br>16        |
| X, P       | WO 03 040219 A (RADIO FREQUENCY SYSTEMS<br>INC ; BUFANDA DAN (US); AUDENAERDE KARL<br>(US) 15 May 2003 (2003-05-15)<br>page 3, line 20 -page 9, line 14<br>page 10, line 14 -page 14, line 12;<br>claims; figures; example | 1-11, 15,<br>16        |

## INTERNATIONAL SEARCH REPORT

ation on patent family members

Internat' Application No

PCT/GB 03/03964

| Patent document<br>cited in search report |    | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
|---|----|---------------------|----------------------------|---------------------|
| US 5866053                                | A  | 02-02-1999          | US 6051174 A               | 18-04-2000          |
| WO 9600610                                | A  | 11-01-1996          | AT 174531 T                | 15-01-1999          |
|   |    |                     | AU 688526 B2               | 12-03-1998          |
|   |    |                     | AU 2800395 A               | 25-01-1996          |
|   |    |                     | CA 2192811 A1              | 11-01-1996          |
|   |    |                     | DE 69506707 D1             | 28-01-1999          |
|   |    |                     | DE 69506707 T2             | 01-07-1999          |
|   |    |                     | DK 767702 T3               | 23-08-1999          |
|   |    |                     | EP 0767702 A1              | 16-04-1997          |
|   |    |                     | ES 2128743 T3              | 16-05-1999          |
|   |    |                     | WO 9600610 A1              | 11-01-1996          |
|   |    |                     | GR 3029531 T3              | 30-06-1999          |
|   |    |                     | JP 3386470 B2              | 17-03-2003          |
|   |    |                     | JP 10502016 T              | 24-02-1998          |
|   |    |                     | US 2002010982 A1           | 31-01-2002          |
|   |    |                     | US 6063138 A               | 16-05-2000          |
|   |    |                     | US 2002073511 A1           | 20-06-2002          |
|   |    |                     | ZA 9505437 A               | 16-02-1996          |
| WO 0197584                                | A  | 20-12-2001          | AU 6984001 A               | 24-12-2001          |
|   |    |                     | CA 2408317 A1              | 20-12-2001          |
|   |    |                     | CN 1436117 T               | 13-08-2003          |
|   |    |                     | EP 1289728 A2              | 12-03-2003          |
|   |    |                     | WO 0197584 A2              | 20-12-2001          |
|   |    |                     | US 2003077346 A1           | 24-04-2003          |
|   |    |                     | US 2002009584 A1           | 24-01-2002          |
| WO 9409913                                | A  | 11-05-1994          | AU 678788 B2               | 12-06-1997          |
|   |    |                     | AU 5540694 A               | 24-05-1994          |
|   |    |                     | BR 9307346 A               | 01-06-1999          |
|   |    |                     | CA 2145626 A1              | 11-05-1994          |
|   |    |                     | EP 0669858 A1              | 06-09-1995          |
|   |    |                     | JP 8503721 T               | 23-04-1996          |
|   |    |                     | MX 9306825 A1              | 31-01-1995          |
|   |    |                     | WO 9409913 A1              | 11-05-1994          |
|   |    |                     | US 5399597 A               | 21-03-1995          |
|   |    |                     | US 5548004 A               | 20-08-1996          |
| US 2002090458                             | A1 | 11-07-2002          | JP 2002225000 A            | 13-08-2002          |
| EP 0370268                                | A  | 30-05-1990          | US 4882107 A               | 21-11-1989          |
|   |    |                     | AT 126752 T                | 15-09-1995          |
|   |    |                     | AU 631381 B2               | 26-11-1992          |
|   |    |                     | AU 4379489 A               | 31-05-1990          |
|   |    |                     | BR 8905509 A               | 29-05-1990          |
|   |    |                     | CA 2001704 A1              | 23-05-1990          |
|   |    |                     | DE 68923931 D1             | 28-09-1995          |
|   |    |                     | DE 68923931 T2             | 04-01-1996          |
|   |    |                     | EP 0370268 A2              | 30-05-1990          |
|   |    |                     | ES 2075841 T3              | 16-10-1995          |
|   |    |                     | GR 3017448 T3              | 31-12-1995          |
|   |    |                     | JP 1960789 C               | 10-08-1995          |
|   |    |                     | JP 2212107 A               | 23-08-1990          |
|   |    |                     | JP 6088255 B               | 09-11-1994          |
|   |    |                     | KR 9507143 B1              | 30-06-1995          |
|   |    |                     | MX 164238 B                | 27-07-1992          |

## INTERNATIONAL SEARCH REPORT

ation on patent family members

Internat Application No

PCT/GB 03/03964

| Patent document<br>cited in search report |   | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
|---|---|---------------------|----------------------------|---------------------|
| EP 0590647                                | A | 06-04-1994          | US 5308648 A               | 03-05-1994          |
|   |   |                     | AT 146988 T                | 15-01-1997          |
|   |   |                     | AU 4871293 A               | 14-04-1994          |
|   |   |                     | BR 9303951 A               | 21-06-1994          |
|   |   |                     | CA 2107302 A1              | 31-03-1994          |
|   |   |                     | DE 69307073 D1             | 13-02-1997          |
|   |   |                     | DE 69307073 T2             | 17-04-1997          |
|   |   |                     | EP 0590647 A1              | 06-04-1994          |
|   |   |                     | ES 2096171 T3              | 01-03-1997          |
|   |   |                     | JP 2552246 B2              | 06-11-1996          |
|   |   |                     | JP 6200044 A               | 19-07-1994          |
| WO 9306731                                | A | 15-04-1993          | US 5120559 A               | 09-06-1992          |
|   |   |                     | AT 157841 T                | 15-09-1997          |
|   |   |                     | DE 69222146 D1             | 16-10-1997          |
|   |   |                     | DE 69222146 T2             | 15-01-1998          |
|   |   |                     | EP 0565651 A1              | 20-10-1993          |
|   |   |                     | JP 6503232 T               | 14-04-1994          |
|   |   |                     | WO 9306731 A1              | 15-04-1993          |
| US 5417992                                | A | 23-05-1995          | WO 9524830 A1              | 21-09-1995          |
| WO 03040219                               | A | 15-05-2003          | WO 03040219 A1             | 15-05-2003          |
|   |   |                     | US 2003087975 A1           | 08-05-2003          |